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Quality Assurance Project Plan

Waitsburg Wastewater Treatment Plant Groundwater Study: Evaluation of Nutrient Loading to the Touchet River

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Quality Assurance Project Plan

Waitsburg Wastewater Treatment Plant Groundwater Study: Evaluation of Nutrient Loading to the Touchet River

November 2009

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ERO – Eastern Regional Office
EAP - Environmental Assessment Program
EOS – Eastern Operations Section
EIM - Environmental Information Management system

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Abstract

In 2007 a Total Maximum Daily Load Study (TMDL) Water Quality Improvement Report was published to address federal Clean Water Act 303(d) listings for pH and dissolved oxygen in the Walla Walla River watershed. The report recommended additional field investigation in several key areas of concern within the watershed to help identify the specific source(s) of elevated nutrients in surface water. This included a recommendation for a nutrient source and loading study at the Waitsburg, Washington municipal wastewater treatment plant (WWTP).

Treated effluent from the Waitsburg WWTP is released to an unlined infiltration wetland immediately adjacent to the Touchet River, a tributary to the Walla Walla River. The wetland is considered in hydraulic continuity with the river. This suggests the possibility that an excess nutrient load could be reaching the river from the infiltration system via subsurface seepage of groundwater into the river. This groundwater study is proposed to determine if this is the case.

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completion of the study, a final report describing the study results will be posted to the Internet.

Background

In 2007 a Total Maximum Daily Load Study (TMDL) Water Quality Improvement Report was published to address federal Clean Water Act 303(d) listings for pH and dissolved oxygen in the Walla Walla River watershed (Joy et al., 2007). The report describes the findings and recommendations that resulted from an extensive field monitoring effort conducted within the basin during 2002 and 2003.

The 2007 improvement report recommended additional field investigation in several key areas of concern within the watershed to help identify the specific source(s) of elevated nutrients observed in surface water. This included a recommendation for a nutrient source and loading study at the Waitsburg, Washington municipal wastewater treatment plant (WWTP)(Figure 1).

During the 2002-2003 TMDL monitoring period, increases in nitrogen, chloride, and alkalinity loads were observed in the Touchet River in the vicinity of the Waitsburg WWTP[1]. These increases could not be explained by local tributary inputs alone (for example from nearby Coppei Creek). Effluent from the Waitsburg WWTP is released to an unlined infiltration wetland in hydraulic continuity with the river (Ecology, 2005; Katsel, 2009). Joy and his co-authors concluded that the facility could be contributing an excess nutrient load to the river via subsurface seepage of groundwater into the river.

Initial Seepage Evaluation

In October 2007, in response to the improvement report recommendations, the Washington State Department of Ecology (Ecology) Environmental Assessment Program conducted a follow-up seepage evaluation on the Touchet River (Tarbutton, 2008). The goal of this evaluation was to help improve the understanding of groundwater and surface water exchange in this portion of the watershed.

A seepage evaluation is a reconnaissance technique used to estimate net gains and losses along discrete reaches of a stream during baseflow conditions. This is accomplished by comparing discharge measurements at upstream and downstream points, while accounting for intervening inflows and outtakes. Unaccountable gains or losses in streamflow are assumed to provide an estimate of the water volume exchange occurring between the stream and the adjoining groundwater system.

Table 1 and Figure 2 summarize the net water exchange estimates from the October 2007 seepage study. The uncertainty interval for each of the exchanges calculated from the discharge data was also estimated using a first-order analysis of measurement accuracy. The uncertainty estimates were calculated using techniques described by Konrad et al. (2003) and Konrad (2006).

[1] The Touchet River is a major tributary of the Walla Walla River. As the limiting nutrient for the Touchet River plant life, excess nitrogen could stimulate excess plant and algae growth that can lead to undesirable dissolved oxygen and pH conditions in the water column (Joy et al., 2007).

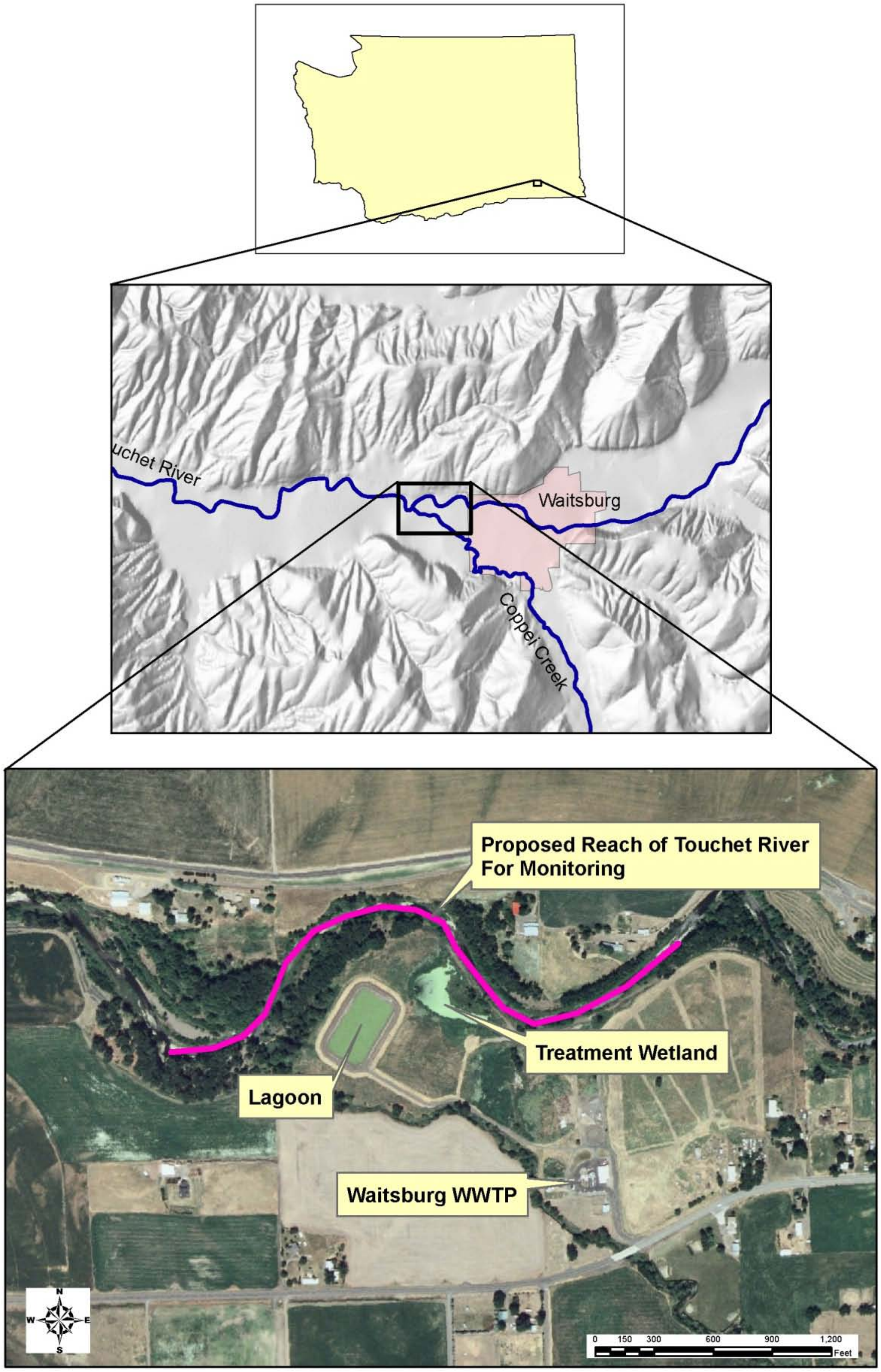


Figure 1. Study Location Map, Walla Walla County, Washington.

Table 1. Touchet River Mainstem Seepage Evaluation – October 25, 2007.

Reach	Station	ID	Station name	Approximate mileage from previous mainstem station	Flow (ft3/sec)	Net gain/loss over reach (ft3/sec)	One-sided 95% uncertainty interval on gain/loss	Unit gain/loss over reach (ft3/sec/mi)
1	1	32NFT00.0	N. Fk. Touchet R. above confluence w/ S. Fk. Touchet R.	-	45			
	2	32SFT00.0	S. Fk. Touchet R. above confluence w/ N. Fk. Touchet R.		4.3			
	3	32B140	Touchet R. mainstem @ Dayton City Park footbridge.	1.35	47 (duplicate avg.)	(2.3)	(5.0)	(1.7)
2	4	32B130	Touchet R. mainstem @ US Highway 12 bridge.	0.40	48	1.0	3.4	2.5
3	5	32PAT00.1	Patit Ck. @ Front St. bridge.		0.03			
	6	32TOU52.2	Touchet R. mainstem above Dayton WWTP outfall.	1.21	52	4.0	5.4	3.3
4	7	32DAYWWTP	Dayton WWTP outfall.		NM			
	8	32TOU52.1	Touchet R. mainstem below Dayton WWTP outfall.	0.05	52	0.0	3.7	0.0
5	9	32TOU51.2	Touchet R. mainstem under Ward Rd. bridge.	1.16	51	(1.0)	(3.6)	(0.9)
6	10	32B120	Touchet R. mainstem at Rose Gulch Rd.	1.94	52 (duplicate avg.)	1.0	3.6	0.5
7	11	32TOU48.4	Touchet R. mainstem @ Lewis and Clark St. Park.	1.42	51	(1.0)	(3.6)	(0.7)
8	12	32B110	Touchet R. mainstem @ county line (staff gage).	2.59	50	(1.0)	(3.6)	(0.4)
9	13	32TOU46.2	Touchet R. mainstem below Lower Hogeye Rd. bridge.	0.34	49 (duplicate avg.)	(1.0)	(3.5)	(3.0)
10	14	32WHI00.1	Whiskey Ck. above confluence w/ Touchet R. mainstem.		0.03			
	15	32WIL00.1	Wilson Ck. above confluence w/ Touchet R. mainstem.		Dry			
	16	32TOU44.2	Touchet R. mainstem @ Highway 12 in Waitsburg.	2.05	52	3.0	5.4	1.5
11	17	32TOU43.5	Touchet R. mainstem above Waitsburg WWTP.	1.09	49	(3.0)	(3.6)	(2.8)
12	18	32WAIWWTP	Waitsburg WWTP.		NM			
	19	32TOU43.0	Touchet R. mainstem below WWTP, above Coppei Ck.	0.42	56	7.0	3.7	17
13	20	32COP00.0	Coppei Ck. above confluence w/ Touchet R.		2.5			
	21	32TOU42.8	Touchet R. mainstem below confluence w/ Coppei Ck.	0.09	57 (duplicate avg.)	(1.5)	(6.1)	(17)

Discharge values in parentheses indicate negative number (losing condition). Positive values indicate gaining condition. Discharge data from Tarbutton (2008).
Shaded cell indicates exchange greater than measurement error confidence interval. All discharge measurements are assumed to have 8% accuracy rating.
NM – not measured

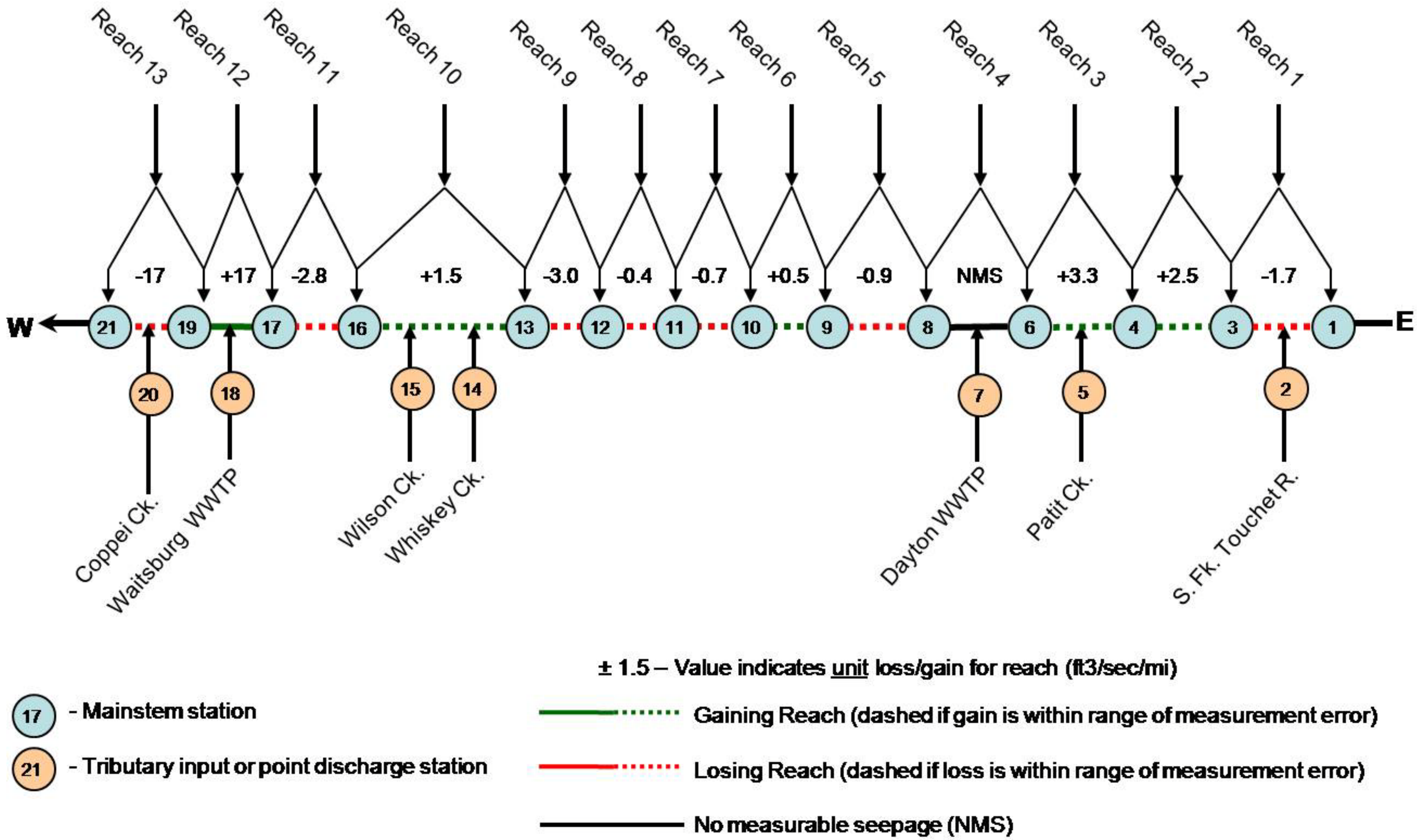


Figure not to scale

Figure 2. Touchet River Seepage Evaluation – October 25, 2007.

The uncertainty analysis suggests that exchange between the Touchet River and the local groundwater system is negligible (i.e., within the range of estimated measurement error) along most of the measured length of the river. One exception, the ~2200 foot long reach that includes the Waitsburg WWTP (Reach 12), showed a significant, unaccounted gain in stream discharge (~7 cfs) that is greater than the estimated uncertainty envelope. This reach also showed an unusually high unit gain in discharge in comparison to the majority of the other reaches evaluated (~17 cubic feet per second per mile). This gain is consistent with discharge and gain estimates made by Joy (1986).

The discharge gain estimated along Reach 12 is significantly larger than the average daily WWTP influent flow rate reported for the past several years (~0.17 mgd; ~0.3 cfs; WPLCS, 2009). This suggests that either the discharge measurements at stations 17 and 19 (Table 1) are less accurate than assumed (i.e. the gain is an artifact of measurement error), or that groundwater transport and seepage of effluent into the river via groundwater flow represents only a portion of the overall gain. Additional field testing is required to further investigate local groundwater and surface water exchange, and determine if this exchange is a source of excess nutrients to the river.

Study Area Description

Physical Setting

Marti (2005) presented the results of field investigations to characterize groundwater/surface water exchange in the Walla Walla watershed, in support of Ecology's TMDL effort. That report provides basin-scale descriptions of the study area, including geologic and hydrogeologic background information.

The Waitsburg WWTP is located adjacent to the south bank of the Touchet River, approximately ½-mile west of the City of Waitsburg, Washington (population ~1230) (Figure 1). Land use immediately surrounding the plant, and on the north side of the river, is predominantly agricultural, with interspersed rural development.

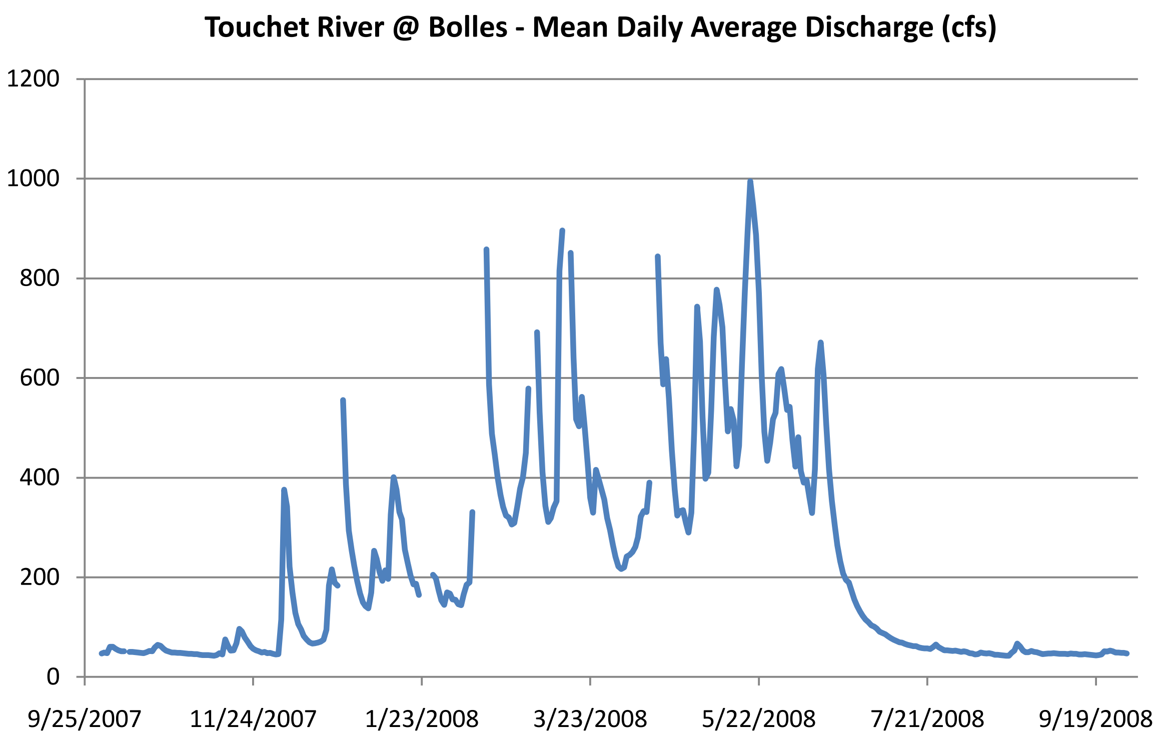
Locally, the Waitsburg WWTP is situated over Holocene-age, alluvial valley-fill sediments deposited by the Touchet River. The sediments are predominately clayey, silty gravels and cobbles. These unconsolidated sediments overlie regional, Miocene-age bedrock units of the Columbia River Basalt group (Frenchman Springs Member of the Wanapum Basalt Formation, and Grande Ronde Basalts). A thin unit of Pleistocene-age loess deposits mantles the foothills adjacent to the river valley (Schuster, 1994; Ecology, 2009).

A typical annual flow hydrograph for the Touchet River is illustrated in Figure 3 (the Bolles station is located ~3 miles downstream of the Waitsburg facility). The baseflow season for the river and the primary period of interest for nutrient loading is between late July and early November.

Site Description

WWTP effluent is currently discharged to an unlined infiltration wetland (~1 acre) located within 100 feet of the river (Figure 1). The wetland is considered to be in hydraulic continuity with the river via groundwater flow (Joy et al., 2007; Ecology, 2005). The water level in the wetland is approximately 4 feet above the summer stage elevation of the Touchet River (Ecology, 2002). An adjacent, plastic-lined lagoon (~1.5 acre) currently provides storage capacity for excess influent during high-flow events. Water is continuously held in the lagoon to suppress vegetation growth (Katsel, 2009).

Prior to 2003, clarified effluent passed through a trickling filter, was routed through the lagoon for secondary clarification, and was then discharged to the infiltration wetland. In the spring of 2003, the treatment process at the WWTP was upgraded to an activated sludge/UV disinfection/ oxidation ditch system, and effluent discharge was re-routed directly to the wetland (Koch, 2009; Katsel, 2009).



Provisional data, Washington State Department of Ecology, Stream Hydrology Unit

Figure 3. Example Annual Streamflow Pattern – Touchet River at Bolles, Washington, Water Year 2008.

The change in treatment process significantly altered the nitrate-to-ammonia ratio of the WWTP effluent (Table 2). Although the nitrate-N effluent concentration reported over the last several years has averaged approximately 14 mg/L, concentrations as high as 85 mg/L have been reported (WPLCS, 2009). Since nitrate is normally transported conservatively in aquifers, there is a concern that excess nitrogen could be moving from beneath the wetland, through the hyporheic zone, and into the water column of the Touchet River.

Table 2. Average Monthly Discharge Monitoring Report (DMR) for Ammonia and Nitrate Effluent Concentrations – Waitsburg WWTP.

Parameter	Oct 1995-Feb 2003	May 2003-Apr 2009
Total Ammonia as Nitrogen (mg/L)	12	0.4
Total Nitrate as Nitrogen (mg/L)	1	16

Data from WPLCS, 2009.

In the 1980s, prior to the construction of the lined lagoon, WWTP effluent was passed through an unlined lagoon positioned south-southeast of the wetland. Facility studies conducted during this period indicated that the old lagoon lost a significant volume of water to the subsurface and may have altered groundwater flow patterns and water quality conditions in this area of the WWTP property (Heffner, 1986). The old lagoon is no longer in use.

An unlined town landfill is reportedly also buried on the WWTP property to the southeast of the wetland. This landfill received waste from the community of Waitsburg, although the years of operation and specific nature of the waste disposed are not documented. Buried waste in the landfill may also affect groundwater quality underlying the property (Katsel, 2009).

No wells are currently present at the Waitsburg WWTP (Katsel, 2009). As a result, groundwater flow directions in the vicinity of the infiltration wetland and surrounding features are unknown. The oxbow configuration of the river (Figure 1) suggests the possibility of a radial (i.e., multi-directional) groundwater flow pattern in this area.

Project Description

This Quality Assurance (QA) Project Plan describes monitoring designed to determine if effluent released to the Waitsburg WWTP infiltration system is a source of significant nutrient loading to the Touchet River via groundwater seepage. The information generated by this study will support further technical analysis and numerical modeling of water quality conditions for the Touchet River.

A variety of field techniques will be employed to (1) characterize local groundwater/surface water interaction patterns during the baseflow period, and (2) describe the quality of the groundwater downgradient of the WWTP infiltration system, just prior to its discharge to the Touchet River. Due to the lack of existing wells at the study site, monitoring of a network of near-shore streambed piezometers and surface water locations in the vicinity of the infiltration system will be used as the primary technical approach for the project. This work will be augmented by the additional surface water monitoring and seepage evaluation work described by Tarbutton (2009).

Organization, Schedule, and Laboratory Budget

Organization

Table 3 presents a list of the personnel involved in this project. All are employees of the Washington State Department of Ecology.

Table 3. Organization of Project Staff and Responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Karin Baldwin Water Quality Program Eastern Regional Office Phone: (509) 329-3472	EAP Client	Clarifies scopes of the project, provides internal review of the QAPP, and approves the final QAPP.
Charles F. Pitz GFF Unit Statewide Coordination Section Phone: (360) 407-6775	Project Manager/ Principal Investigator	Writes the QAPP, oversees field sampling and transportation of samples to the laboratory, conducts QA review of data, analyzes and interprets data, enters data into EIM, and writes the draft report and final report.
Scott Tarbutton/Tighe Stuart Spokane Office Eastern Operations Section Phone: (509) 329-3453	Field Assistants	Help install piezometers, collect samples, and record field information.
Martha Maggi GFF Unit Statewide Coordination Section Phone: (360) 407-6453	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra Statewide Coordination Section Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Gary Arnold Eastern Operations Section Phone: (509) 454-4244	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

GFF – Groundwater/Forests & Fish.
EAP – Environmental Assessment Program.
EIM – Environmental Information Management system.
QAPP – Quality Assurance Project Plan.

Schedule

Table 4 presents a proposed schedule for completing field and laboratory work, data entry into EIM, and project reports.

Table 4. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	October 2009	Charles F. Pitz
Laboratory analyses completed	November 2009	
Environmental Information System (EIM) database		
EIM user study ID	CHPI004	
Product	Due date	Lead staff
EIM data loaded	November 2009	Charles F. Pitz
EIM QA	June 2010	Martha Maggi
EIM complete	August 2010	Charles F. Pitz
Final report		
Author lead	Charles F. Pitz	
Schedule		
Draft due to supervisor	April 2010	
Draft due to client/peer	May 2010	
Draft due to external	June 2010	
Final (all reviews done) due to publications coordinator	July 2010	
Final report due on web	August 2010	

Laboratory Budget

All samples collected for laboratory analysis will be submitted to Ecology's Manchester Environmental Laboratory (MEL). Table 5 presents a proposed laboratory budget for the project. Estimated costs assume a 50% discount for MEL services.

Table 4. Estimated Laboratory Budget.

Parameter	Cost per Sample	Number of Field Samples[A]	Estimated Cost
Total dissolved phosphorus	$18	42	$756
Orthophosphate -P	$15	42	$630
Nitrate+nitrite-N	$13	42	$546
Ammonia-N	$13	42	$546
Chloride	$13	42	$546
Total dissolved solids	$11	42	$462
Sodium	$28	42	$1176
Sulfate	$13	42	$546
Dissolved organic carbon	$35	42	$1470
Base/Neutral/Acids (BNAs) Semivolatiles (no TICs)	$250	4	$1000
		Total Cost	$7678

[A]Assumptions:
-8 sampled piezometers, 4 surface water grab samples, and 2 QA samples per event for 3 sampling events.
-3 stations (and one field blank) will be sampled for BNAs for 1 sampling event.
-All samples field-filtered water.

Quality Objectives

A primary objective of this study is to provide data that are representative of field conditions. Measurements of water quality and hydrologic conditions may be used to:

- Identify probable locations of groundwater seepage to the Touchet River related to the Waitsburg WWTP infiltration system.
- Characterize the water quality of groundwater discharge to the Touchet River downgradient of the infiltration system.
- Develop nutrient loading estimates.
- Support further analysis using the QUAL2Kw water quality model (Joy et al., 2007).

Tables 6 and 7 present the measurement quality objectives (MQOs) that will be used when assessing data quality of field and laboratory data, respectively. Manchester Environmental Laboratory is expected to meet quality control requirements for the laboratory methods selected for the project.

Table 5. Field Analyte Measurement Quality Objectives.

Analyte	Accuracy	Required Reporting Limit	Field Replicate Precision
pH	±0.15 s.u.	1-14 s.u.	<10% RPD
Temperature	±0.2°C	1 – 40°C	<10% RPD
Specific conductance	±10 µmho/cm	1 µmho/cm	<10% RPD
Oxidation/Reduction Potential (ORP)	±20 mV	10 mV	<20% RPD
Dissolved oxygen (probe)	±0.2 mg/L	1 mg/L	<20% RPD
Dissolved oxygen (chemical)	~±0.5 mg/L @ 1-12 mg/L ~±0.05 mg/L @ 0.025-1 mg/L	0.025 mg/L	<25% RPD
Ferrous iron	~±5 µg/L @ 0-1 mg/L ~±0.5 mg/L @ 1-10 mg/L	0.050 mg/L	<25% RPD
Nitrate-N	±30% over range (0.40-3.00 mg/L)	0.4 mg/L	<30% RPD
Water level	±0.01 ft	n/a	<10% RPD

Table 6. Laboratory Analyte Measurement Quality Objectives.

Analyte	LCS % Recovery	Lab Duplicate Precision RPD	Matrix Spikes % Recovery	Matrix Spike RPD	Surrogate Recoveries (% Recovery)	Required Reporting Limit*	Field Replicate Precision
Total dissolved phosphorus	80-120	≤20	75-125	≤20	NA	5 µg/L	<15% RSD
Orthophosphate-P	80-120	≤20	75-125	≤20	NA	3 µg/L	<15% RSD
Nitrate+nitrite-N	80-120	≤20	75-125	≤20	NA	0.022 mg/L	<15% RSD
Ammonia-N	80-120	≤20	75-125	≤20	NA	0.01 mg/L	<15% RSD
Total dissolved solids	80-120	≤20	75-125	≤20	NA	1 mg/L	<10% RSD
Chloride	90-110	≤20	75-125	≤20	NA	0.1 mg/L	<10% RSD
Sodium	85 - 115	≤20	75 -125	≤20	NA	0.05 mg/L	<10% RSD
Sulfate	80 -120	≤20	75-125	≤20	NA	0.4 mg/L	<15% RSD
Dissolved organic carbon	80 -120	≤20	75-125	≤20	NA	1 mg/L	<25% RSD
Base/Neutrals/Acids (BNAs) Semivolatiles	40-150	≤50	50-150	≤40	10-150[(A)]	1-5 µg/L	NA

NA – not applicable

*The stated reporting limit is for undiluted, field-filtered water samples. In cases where the sample volume submitted to the laboratory is too small for analysis by the method requested, a dilution may be performed by the laboratory, at the discretion of the project manager. It is recognized that in such cases, the reporting limit will increase by the factor of dilution.

[(A)]Surrogate recoveries are compound specific.

Study Design

A suite of field techniques will be used for this study. The locations of monitoring points will be dependent on the findings of earlier field observations and measurements. The number and location of instream monitoring devices will also be strongly dictated by the suitability of streambed sediments for equipment installation.

The study approach proposed for this project is described below:

1. Conduct an initial reconnaissance survey of streambed porewater temperature conditions along the Touchet River upstream, adjacent to, and downstream of the WWTP infiltration system. The goal of this reconnaissance work is to identify areas of probable groundwater inflow to the river and to prioritize locations for monitoring devices.
2. Install a network of small-diameter (1” inner diameter) piezometers in the near-shore streambed sediments upstream of, adjacent to, and downstream of the WWTP infiltration system. Piezometer locations will be guided in part by the results of the streambed temperature reconnaissance, and preliminary water quality measurements described below. One piezometer will be installed far upstream, and one on the river bank opposite (north) of the WWTP to provide background condition data.
3. After installation, develop and purge piezometers, and collect preliminary field measurements of groundwater dissolved oxygen and nitrate conditions using a field photometer.
4. On the basis of the temperature reconnaissance and photometer results, install and instrument several additional piezometers for continuous thermal monitoring in areas of key concern. Thermal monitoring will provide continuous data on timing and direction of exchange of groundwater and surface water during the baseflow season. Prior to developing thermal monitoring piezometers, conduct constant-head injection tests to determine the bulk permeability of the streambed sediments (Pitz, 2006).
5. Periodically monitor and sample streambed piezometers during the baseflow season. Monitoring events will occur once in August, September, and October of 2009. All piezometers will be monitored for:
    - Field parameters
        - vertical hydraulic gradient
        - temperature
        - pH
        - specific conductance
        - dissolved oxygen
        - oxidation-reduction potential
        - ferrous iron
    - Orthophosphate-P
    - Total dissolved phosphorus

- Nitrate+nitrite as N[2]
- Ammonia as N
- Total dissolved solids
- Chloride
- Sodium
- Sulfate
- Dissolved organic carbon

6. Monitor and sample surface water quality in the Touchet River, the WWTP infiltration wetland, and the WWTP lagoon to provide a baseline comparison for groundwater sample results. Also collect one opportunistic grab sample of river bank groundwater seepage if encountered during field work.
7. During one monitoring round, collect additional water samples from 1 piezometer, 1 groundwater seep, and the facility wetland for analysis for base/neutral/acids (BNAs) semivolatiles. Monitoring for BNAs will help to evaluate the degree of anthropogenic impact on the water quality of groundwater and surface water exchange, and may assist source identification efforts.
8. Conduct additional synoptic seepage evaluations and surface water quality sampling on the Touchet River to provide additional information near the Waitsburg WWTP (Tarbutton, 2009).

[2] Dissolved nitrite concentrations in groundwater systems are typically very low. Nitrate+nitrite-N groundwater results are typically considered equivalent to Nitrate-N results.

Testing and Sampling Procedures

Streambed temperature reconnaissance will be accomplished by inserting a long-shaft K-type temperature probe into the streambed sediments until refusal (not greater than 18" deep). Temperature measurements will be collected along an approximately 3000-foot (900-meter) long section of the Touchet River upstream, adjacent to, and downstream of the WWTP infiltration system. Measurements will be collected approximately every 30 feet (10 meters), within wading depth of shoreline, while maintaining a consistent water depth.

Installation, development, and field monitoring of instream piezometers will follow techniques equivalent to those outlined in Sinclair and Pitz (2009). Permeability testing of piezometers will be conducted per the procedures outlined in Pitz (2006). Purging and sampling of all piezometers (low-flow) will follow techniques equivalent to those described by Pitz (2002) and Pitz et al. (2005). Grab samples from the lagoon, wetland, river, and groundwater seep will be collected per methods outlined by Joy (2006). All groundwater and surface water samples will be field filtered at 0.45 microns to distinguish dissolved phase concentrations likely to be mobile in the groundwater environment.

A field photometer will be used for collecting end-of-purge measurements of field-sensitive parameters (ferrous iron and dissolved oxygen), and for rapid reconnaissance measurements of nitrate-N. Photometric tests will be run per manufacturer's guidelines. Prior to measurement, the photometer will be manually zeroed using a light shield and manufacturer-supplied, distilled-water zeroing ampoule. Samples for photometric analysis are collected by immersing the appropriate test kit vacuum ampoule in the sample stream for several minutes until the ampoule temperature is equilibrated with the sample water.

In cases of excess turbidity, photometric analysis may be run on a filtered aliquot to reduce spectral interference. Sample measurements will be conducted at the end of a test-specific, pre-programmed wait time to allow adequate reaction between test reagents and sample, for proper color development. Duplicate photometer measurements will be collected at a 10% frequency.

The field photometer will be calibrated for dissolved oxygen measurement by comparing and recording measurement results of an air-exposed de-ionized water sample to results collected on the same sample by a calibrated membrane probe (one-point water-saturated air calibration). Confirmation measurements of dissolved oxygen will be collected by photometer at the end of piezometer purge for all stations where the membrane probe reports a concentration of $\leq$2 mg/L. No calibration procedures will be employed for photometric analysis of ferrous iron or reconnaissance mapping of nitrate-N.

Continuous thermal profiling devices will be deployed using methods described by Sinclair and Kardouni (2009) and Bilhimer and Stohr (2008).

A summary of the project measurement methods for both field and water quality analyses is presented in Table 8.

Tables 9 and 10 present sample handling protocols. Samples will be collected following Ecology's Environmental Assessment Program safety and chemical hygiene protocols. Clean sample containers, pre-preserved when appropriate, will be supplied by MEL. Samples will be shipped to MEL in chilled, secured coolers on the day of collection via United Parcel Service next-day air package express from the Walla Walla airport.

Table 7. Summary of Project Measurement Methods.

Analyte[A]	Equipment Type/Test Method[B][C]	Reporting Limit[D]
Field		
pH	Electrode probe[E] - EPA Method 150.1	0.1 SU
Specific conductance	Electrode-pair probe[E] - EPA Method 120.1	1 µS/cm
Oxidation-reduction potential (ORP)	Electrode probe[E] – SM2580-B	±2000 mV measurement range; 1 mV resolution
Dissolved oxygen	Electrochemical probe EPA Method 360.1 (during purge)	0.1 mg/L
	CHEMetrics V-2000 field photometer (end of purge confirmation) (test kits K-7503 and K7513)	0.2 mg/L
	CHEMetrics Colorimetric – Rhodazine D Method (low concentration end of purge confirmation – test kit K-7501)	0.025 mg/L
Ferrous iron	CHEMetrics V-2000 field photometer (test kit K-6203)	0.2 mg/L
Nitrate-N	CHEMetrics V-2000 field photometer (test kit K-6923)	0.4 mg/L
Water level	Small diameter e-tape/ engineer's rule	±0.01 feet
Temperature	Type K long-shaft thermocouple probe and meter/ Recording thermistors	-20°C to +50°C
Laboratory - MEL		
Total dissolved phosphorus	SM 4500-P F	5 µg/L
Orthophosphate-P	SM 4500-P G	3 µg/L
Nitrate+nitrite-N	EPA Method 300.0[F]	0.022 mg/L as N
Ammonia-N	SM 4500-NH3 H	0.01 mg/L as N
Chloride	EPA Method 300.0/SM 4110C	0.1 mg/L
Sodium	EPA Method 200.7	0.05 mg/L
Sulfate	EPA Method 300.0	0.4 mg/L
Dissolved organic carbon	EPA 415.1	1 mg/L
Base/Neutral/Acids (BNAs) Semivolatiles	EPA Method 8270[G]	1 – 5 µg/L

(A) All samples will be field-filtered water matrix.
(B) SM – Standard Method (APHA, AWWA, and WEF, 1998).
(C) ASTM – American Society for Testing and Materials method.
(D) The reporting limit is for an undiluted sample. The reporting limit increases by the factor of dilution in cases where a sample requires dilution.
(E) Probe to be used with a WTW multi-line 197i meter.
(F) MEL may analyze samples using SM4500-NO3 I method, as necessary, in consultation with the project lead.
(G) See Appendix B for list of analytes for semivolatile (BNA) analysis by EPA Method 8270

Table 8. Container, Preservation, Handling, and Holding Time Requirements.

Analyte	Container Type	Sample Handling	Preservation	Holding Time
Total dissolved phosphorus	60 ml clear poly (pre-acidified)	Field filter at 0.45 µm	Adjust pH <2 with HCl and cool to <6°C	28 days
Orthophosphate-P	125 ml amber w/m Nalgene	Field filter at 0.45 µm	Cool to <6°C	48 hours
Nitrate+nitrite-N	500 ml poly [(A)]	Field filter at 0.45 µm	Cool to <6°C	48 hours
Ammonia-N	125 ml w/m clear Nalgene (pre-acidified)	Field filter at 0.45 µm	Adjust pH <2 with H_2SO_4 and cool to <6°C	28 days
Total dissolved solids	500 ml poly[(A)]	Field filter at 0.45 µm	Cool to <6°C	7 days
Chloride	500 ml poly[(A)]	Field filter at 0.45 µm	Cool to <6°C	28 days
Sodium	500 ml HDPE	Field filter at 0.45 µm	Adjust pH <2 with HNO_3 and cool to <6°C	6 months
Sulfate	500 ml poly[(A)]	Field filter at 0.45 µm	Cool to <6°C	28 days
Dissolved organic carbon	60 ml clear poly (pre-acidified)	Field filter at 0.45 µm	Adjust pH <2 with HCl and cool to <6°C	28 days
Base/neutral/acids (BNAs) semivolatiles	1 gallon glass jar w/ Teflon lined cap	Field filter at 0.45 µm	Cool to <6°C	7 days

[(A)]Chloride, nitrate+nitrite-N, TDS, and sulfate samples will be combined in a common container.

Quality Control Procedures

Field

Portable equipment used for measurement of field parameters (primarily during piezometer purge) will be pre- and post-calibrated per manufacturer's instructions, using standard calibration solutions or reference tests. Recording thermistors will be pre- and post-calibrated using a water bath, following techniques described by Sinclair and Kardouni (2009).

To assist in evaluating the variability introduced into the samples results by the combination of field and laboratory influences, one split replicate sample set will be collected each sampling round. Replicate samples will be submitted to the laboratory as 'blind' samples and analyzed for all target parameters listed above. The first replicate sample set location will be randomly selected. Subsequent replicates will be located to provide information over the range of concentrations observed during previous sampling. Replicate measurements of all field parameters (including photometric analyses) will be collected at a rate of 1 replicate per 10 samples.

A field-equipment blank will be collected at the beginning of each sampling round to determine the bias introduced into the analytical results by the sample-contact equipment and field handling. Equipment blanks will be collected by pumping laboratory-supplied, reagent-grade de-ionized (DI) water through the sampling system using new parts for all contact portions of the system (e.g., tubing, fittings, filters, and sample containers). Equipment blanks will be submitted to the laboratory as blind samples and will be analyzed for all target parameters.

Additional field quality control measures used to minimize the risk of sample contamination (particularly low-volume profile samples) include (1) the use of clean sampling gloves for each sample set, (2) the use of small volume sample equipment, (3) thorough equipment decontamination between sets, and (4) pre-rinsing of sample contact equipment with sample water prior to collection to a container.

Laboratory

Routine laboratory quality control testing will be used to estimate the accuracy, precision, and bias introduced by laboratory procedures. The results of this testing will be reported to the project lead for data analysis (MEL, 2008). MEL's quality control sampling and test procedures are outlined in detail in their Quality Assurance Manual (MEL, 2006).

Data Management Procedures

Field measurement data and observations will be entered into a field book on waterproof paper, using standardized field sheets. Sampling stations will be identified by a unique ID number and recorded on containers, field notes, and chain-of-custody paperwork. Before leaving site locations, data will be checked for legibility and completeness. Pertinent field data will be transferred from field notes to electronic format as appropriate, using Microsoft Office EXCEL2007 spreadsheets or ACCESS2007 database programs. Temperature data collected by recording thermistors will be downloaded directly to a handheld data storage device and post-processed using the manufacturer's software.

Sampling locations will be recorded using a hand-held Global Positioning System (GPS) unit, as well as field orthophotos. Final station position will be reconciled to digital orthophotography in a geographic information system software package.

Analytical data from MEL will be stored in electronic format in their laboratory data management system (LIMS). After the data are verified, they will be summarized in case narratives and provided to the project manager.

Field and laboratory data for the project will be entered into Ecology's EIM system. Laboratory data will be downloaded directly into EIM from the LIMS system. Data entry into EIM is conducted using established data entry business rules. The EIM data will be reviewed by the project manager, staff entering the data (if different than the project manager), and an independent reviewer.

Audits and Reports

MEL participates in performance and system audits of their routine procedures. Reported results of these audits are available on request. Ecology's Accreditation Program establishes whether the laboratory has the capability to provide accurate and defensible data. To demonstrate the laboratory's ability to provide accurate and defensible data, the accreditation involves an evaluation of the laboratory's quality system, staff, facilities, equipment, test methods, records, and reports.

A technical report will be prepared documenting the study procedures, findings, and recommendations. The report will include a Quality Assurance evaluation describing data acceptability and qualification. The final report will undergo technical peer review by staff with appropriate expertise, who are not directly connected to the project. Publication of the final report is planned for June 2010.

Data Verification

Data verification is a review process to assess the quality and completeness of analytical datasets.

Verification of laboratory data is normally performed by a MEL unit supervisor or an analyst experienced with the analytical method(s) of interest. Laboratory-generated data reduction, review, and reporting will follow the procedures outlined in MEL's Lab Users Manual (MEL, 2008) and Quality Assurance Manual (MEL, 2006). Data will be examined for errors, omissions, and compliance with quality control acceptance criteria; data qualifiers will be assigned where necessary. Findings of the data verification effort will be documented in a case narrative prepared by the appropriate MEL staff member. The case narrative will be forwarded to the project manager for use during data evaluation.

Verification of field-generated measurements is accomplished through review of field note completeness and accuracy, as well as evaluation of field quality assurance test results. Data received from LIMS will be checked for omissions against the "Request for Analysis" forms by the field lead.

Data Usability Assessment

The data usability review involves a detailed evaluation of the project data package using best professional judgment and statistical analysis to determine if the project MQOs have been met. The project manager will compare verified data (both field and laboratory) against established standards for acceptable precision and bias, by evaluation of MEL case narratives and blind quality control data results. As appropriate, the project manager will assign additional data qualifiers where necessary or reject data from further use.

The project manager will evaluate all data generated during the study to determine if the information is of acceptable quality, is complete, is properly qualified where appropriate, and can be used for the project objectives. The final report for the project will discuss data quality, usability, and limitations.

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Appendix A. Glossary, Acronyms, and Abbreviations

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that fall short of state surface water quality standards, and are not expected to improve within the next two years.

Baseflow: The component of total streamflow that originates from direct groundwater discharges to a stream.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Effluent: The treated outflow from a sewage treatment system.

Gaining condition/reach: A defined length of a river or stream that *gains* flow by seepage of water (inflow) *from* the adjacent groundwater system.

Groundwater: Water in the subsurface that saturates the rocks and sediment in which it occurs. The upper surface of groundwater saturation is commonly termed the water table.

Hydraulic gradient: The difference in hydraulic head between two measuring points, divided by the distance between the two points.

Hyporheic: The area beneath and adjacent to a stream where surface water and groundwater intermix.

Losing condition/reach: A defined length of a river or stream that *loses* flow by seepage of water (outflow) *to* the adjacent groundwater system.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Nutrient: Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

Porewater: The water filling the spaces between grains of sediment.

Reach: A specific portion or segment of a stream.

Synoptic: Simultaneous.

Thermistor: An electronic device that uses semiconductors to measure temperature.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Water Year: October 1 – September 30.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
GPS	Global Positioning System
LCS	Laboratory control standard
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NPDES	(See Glossary above)
QA	Quality assurance
RPD	Relative percent difference
RSD	Relative standard deviation
TMDL	(See Glossary above)
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
ft	feet
g	gram, a unit of mass
m	meter
mgd	million gallons per day
mg/L	milligrams per liter (parts per million)
mL	milliliters
mV	millivolt
s.u.	standard units
µg/L	micrograms per liter (parts per billion)
µm	micrometer
µmhos/cm	micromhos per centimeter
µS/cm	microsiemens per centimeter, a unit of conductivity

Appendix B. List of Analytes for Semivolatile Analysis by EPA Method 8270

Benzoic Acid [1]
Benzyl Alcohol
Bisphenol A
Butylbenzylphthalate
4-Bromophenyl-Phenylether
Di-N-Butylphthalate
Caffeine
Cholesterol [1]
4-Chloro-3-Methylphenol
4-Chloroaniline [1]
Bis(2-Chloroethoxy) Methane
Bis(2-Chloroethyl) Ether
Bis(2-Chloroisopropyl) Ether
2-Chloronaphthalene
2-Chlorophenol
4-Chlorophenyl-Phenylether
3B-Coprostanol [1]
3,3'-Dichlorobenzidine [1]
1,2-Dichlorobenzene [1]
1,3-Dichlorobenzene [1]
1,4-Dichlorobenzene [1]
2,4-Dichlorophenol
2,4-Dimethylphenol [1]
2,4-Dinitrophenol [1]
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1,2-Diphenylhydrazine
2-Fluorophenol
Hexachlorobenzene
Hexachlorobutadiene [1]
Hexachlorocyclopentadiene[1]
Hexachloroethane [1]
Isophorone
p-Isopropyltoluene [1]
4,6-Dinitro-2-Methylphenol[1]
2-Methylphenol [1]
4-Methylphenol [1]
2-Nitroaniline
3-Nitroaniline [1]
4-Nitroaniline [1]
Nitrobenzene
2-Nitrophenol

4-Nitrophenol [1]
N-Nitroso-Di-N-Propylamine
N-Nitrosodiphenylamine
N-Nitrosodimethylamine
4-Nonyl Phenol [1]
Pentachlorophenol [1]
Bis (2-Ethylhexyl) Phthalate
Diethylphthalate
Dimethylphthalate
Di-N-Octyl Phthalate
Phenol
Pyridine
Triclosan
1,2,4-Trichlorobenzene[1]
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol

[1] These compounds have inconsistent and poor recoveries.

Surrogates

D4-2 Chlorophenol
1,2-Dichlorobenzene-D4
2-Fluorobiphenyl
D5-Nitrobenzene
D5-Phenol
D10-Pyrene
D14-Terpenyl